EXPERIMENTAL STUDIES

A MODEL OF PHASE RELATIONS IN THE SYSTEM $MgO-SiO_2-H_2O-CO_2$ AND PREDICTION OF THE COMPOSITIONS OF LIQUIDS COEXISTING WITH FORSTERITE AND ENSTATITE

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Abstract. A comprehensive model has been developed for the system $MgO-SiO_2-H_2O-CO_2$ on the basis of experimental studies, Schreinemaker's rules, and thermodynamic data. The assemblage forsterite plus enstatite is predicted to melt in the presence of vapor of any H_2O/CO_2 ratio at low pressures, in the presence of vapor whose H_2O/CO_2 ratio is buffered by the presence of magnesite at intermediate pressures, and at a vapor-absent eutectic with brucite and magnesite at high pressures. The composition of the liquid at the solidus for a bulk composition of forsterite plus enstatite plus a small amount of volatiles with a 3/1 H_2O/CO_2 ratio changes from enstatite-quartz normative at 20 kbar, to periclase-forsterite normative at 50 kbar, to forsterite-enstatite normative at 90 kbar and greater pressures. Forsterite cannot coexist with H_2O-CO_2 vapor at pressures greater than 90 kbar. Thus all melting in the earth's mantle at higher pressures must be vapor-absent.

Introduction

In the Proceedings of the First International Kimberlite Conference Eggler (1975) reported on experimental studies in the system $MgO-SiO_2-H_2O-CO_2$ at 20 kbar and Mysen and Boettcher (1975) discussed experimental results on the effects of H_2O and CO_2 on the melting of peridotite at 20 kbar. We have combined their contributions with other phase equilibrium studies to construct a model of phase equilibria in the system $MgO-SiO_2-H_2O-CO_2$ at pressures up to 100 kbar, where the relationships described at 20 kbar are replaced by more complex phase equilibria involving stable hydrates and carbonates. The model outlined here is described in detail in the papers of Ellis and Wyllie (1978a,b,c). The salient features of phase relations in the ternary systems $MgO-H_2O-CO_2$, $MgO-SiO_2-CO_2$, and $MgO-SiO_2-H_2O$ will be discussed, followed by a summary of the quaternary phase relations and the processes of melting and crystallization.

The System $MgO-H_2O-CO_2$

The phase relations of brucite in the system $MgO-H_2O$ are analogous to those determined by Huang and Wyllie (1976) for magnesite in the system $MgO-CO_2$ (see Figure 1). The position of the reaction

$$\text{Brucite} \rightarrow \text{Periclase} + H_2O \qquad (1)$$

has been predicted on the basis of the experimental studies of Walter et al. (1962), Barnes and Ernst (1963), and Irving et al. (1977), thermochemical data, and water fugacities predicted by the modified Redlich-Kwong equation of state (Holloway, 1977). We estimate that reaction 1 maintains a positive P-T slope until brucite melts at the invariant point (MC), at which brucite, periclase, liquid, and vapor coexist. The invariant point (MC) is located near 58 kbar and 1310°C. At pressures greater than or equal to that of point I, where the reaction

$$\text{Magnesite} + \text{Brucite} \rightarrow \text{Periclase} + \text{Vapor} \qquad (2)$$

meets the solidus, brucite and magnesite melt together at a eutectic. The melting model derived by Bradley (1962) for the system $Ca(OH)_2-CaCO_3$ has been used to predict that the composition of the eutectic liquid is 73 mole percent $Mg(OH)_2$ plus 27 mole percent $MgCO_3$. At temperatures below the solidus the composition of vapor coexisting with magnesite-bearing assemblages is buffered.

The System $MgO-SiO_2-H_2O$

The topology for the system $MgO-SiO_2-H_2O$ shown in Figure 2 was derived on the basis of numerous studies of subsolidus reactions, (especially those of Bowen and Tuttle (1949), Chernosky (1976), Evans et al. (1976), Greenwood (1963, 1971), Johannes (1968), Kitahara et al. (1966), and Scarfe and Wyllie (1967)), and from studies

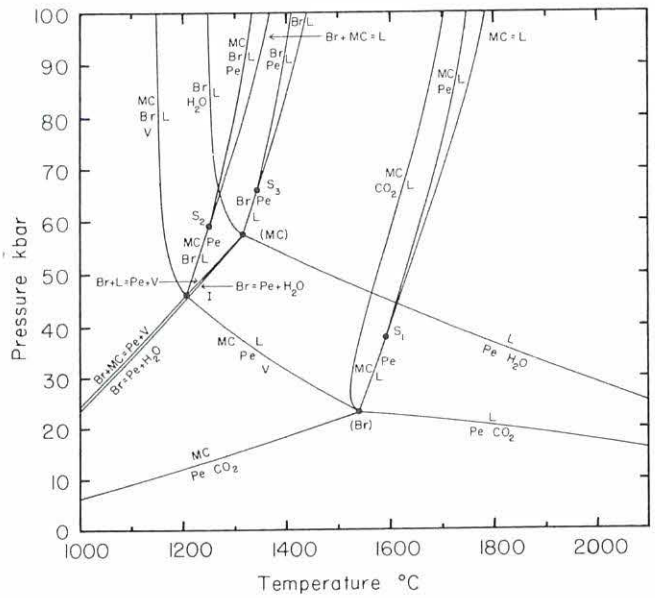

Figure 1. P-T net for the system $MgO-H_2O-CO_2$. Abbreviations used in Figures are Pe = MgO, Br = $Mg(OH)_2$, MC = $MgCO_3$, Q = SiO_2, En = $MgSiO_3$, Fo = Mg_2SiO_4, L = liquid, V = mixed H_2O-CO_2 vapor, H_2O = pure H_2O vapor, CO_2 = pure CO_2 vapor.

of melting relations in this system and related systems (by Eggler (1975), Hodges (1973), Kushiro et al. (1968), Mysen and Boettcher (1975a,b), and Nakumura and Kushiro (1974)). The subsolidus reactions 1 and

$$\text{Brucite} + \text{Enstatite} \rightarrow \text{Forsterite} + H_2O \quad (3)$$

intersect the solidus respectively at the invariant point (En,Q) at about 45 kbar and 1250°C, and the invariant point (Pe,Q) at about 1200°C and 90 kbar. The work of Yamamoto and Akimoto (1977) indicates that the hydrous magnesium silicates, particularly hydroxyl-clinohumite, are not stable at the temperature of the solidus in this system, and thus need not be considered. We assume that the hydrous melting reactions maintain a slight negative slope throughout the range of pressure considered. Near the solidus forsterite plus enstatite coexist with water vapor at low pressures and with brucite at high pressures. At high temperatures water is dissolved in the silicate liquid coexisting with forsterite plus enstatite. If sufficient H_2O is available at pressures greater than 90 kbar, all forsterite will react to form enstatite plus brucite. The assemblage forsterite plus enstatite can not coexist with H_2O at pressures greater than that of the invariant point (Pe,Q).

The System $MgO-SiO_2-CO_2$

The phase equilibria of this system were modeled by Wyllie and Huang (1976). The subsolidus and melting reactions involving magnesite in the system $MgO-SiO_2-CO_2$ take place at higher temperatures and lower pressures than the analogous reactions involving brucite in the system $MgO-SiO_2-H_2O$. The solidus has a positive P-T slope above 25 kbar. Near the solidus of this system, forsterite plus enstatite coexist with CO_2 vapor at low pressure, with magnesite at high pressure, and with silicate liquids containing dissolved CO_2 at temperatures above the solidus. In analogy to the system $MgO-SiO_2-H_2O$, CO_2 may exist as a vapor at high pressures only if all forsterite has been reacted to enstatite plus magnesite.

The System $MgO-SiO_2-H_2O-CO_2$

A model for the system $MgO-SiO_2-H_2O-CO_2$ has been derived from the ternary systems described above. Those reactions which involve the assemblage forsterite plus enstatite are shown in Figure 4. The assemblage forsterite plus enstatite may coexist with a vapor phase only in the low P-T region enclosed by heavy lines. The composition of the vapor phase in the univariant reaction

$$\text{Magnesite}+\text{Forsterite}+\text{Vapor} \rightarrow \text{Enstatite}+\text{Liquid} \quad (4)$$

is buffered by the intersection of the divariant subsolidus reaction surface

$$\text{Magnesite} + \text{Enstatite} \rightarrow \text{Forsterite} + \text{Vapor} \quad (5)$$

with the solidus surface. P-T-X_{CO_2} calculations for reaction 5 show that the vapor present at the solidus must be rich in H_2O at all pressures significantly greater than that of the invariant point labeled A in Figure 4. At pressures

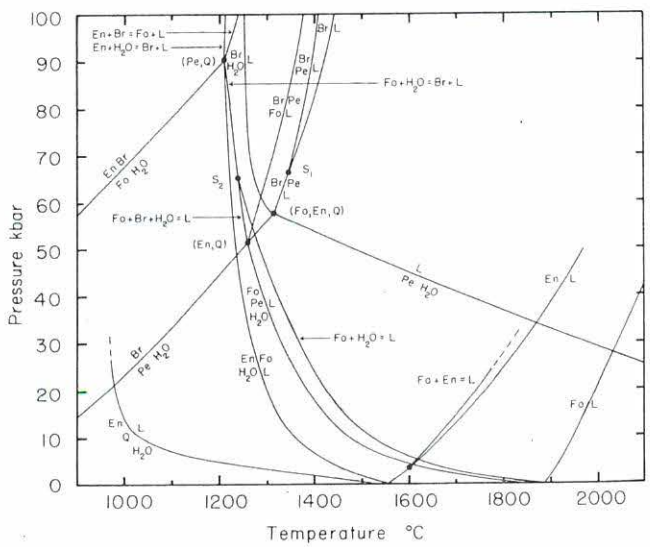

Figure 2. P-T net for the system $MgO-SiO_2-H_2O$.

greater than 90 kbar forsterite is not stable in the presence of vapor of any composition. Forsterite will react with vapor to form enstatite plus magnesite plus brucite until either the vapor or the forsterite is consumed.

The temperature maximum on the solidus surface, shown in Figure 4 as a dashed line, is the locus of isobaric thermal maxima on the reaction

Forsterite + Enstatite + Vapor → Liquid. (6)

It does not exist at pressures below 35 kbar. The temperature maximum originates in the system $MgO-SiO_2-CO_2$ when the rapidly increasing solubility of CO_2 in the silicate liquid which coexists with forsterite and enstatite, associated with the intersection of the subsolidus reaction 5 with the solidus, causes a rapid decrease in the temperature of reaction 6. The thermal maximum on the solidus surface which corresponds to the forsterite-vapor join then begins to migrate away from the CO_2 edge of the $MgO-SiO_2-H_2O-CO_2$ system with increasing pressure. Associated with the thermal maximum on the forsterite-vapor solidus there is a thermal ridge on the vapor-saturated liquidus surface. The forsterite-enstatite boundary on the vapor-saturated liquidus surface traverses this ridge passing through a thermal maximum that chemographic relations show must be located between the forsterite-vapor and the enstatite-vapor joins. As the liquidus ridge retreats from the side forsterite-CO_2 with increasing pressure the

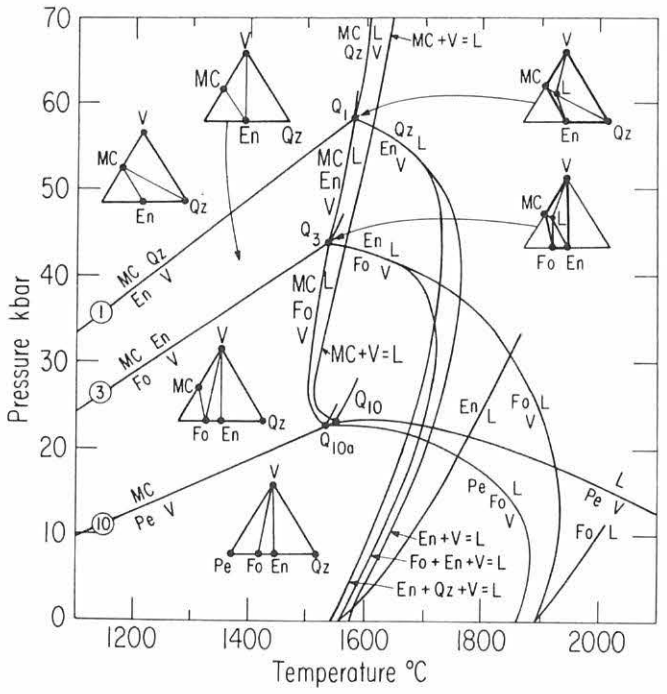

Figure 3. P-T net showing vapor-present univariant reactions in the system $MgO-SiO_2-CO_2$ (Wyllie and Huang, 1976).

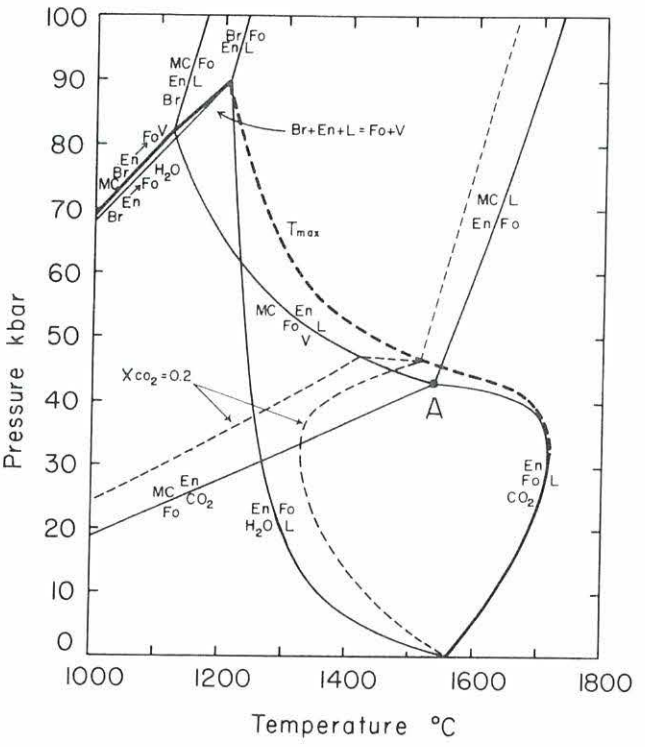

Figure 4. Partial P-T net for the system $MgO-SiO_2-H_2O-CO_2$. Only reactions involving the assemblage forsterite plus enstatite are shown. Vapor may coexist with forsterite plus enstatite only in the P-T region enclosed by the heavy lines. The heavy dashed line shows the position of the thermal maximum on reaction 6.

thermal maximum on the forsterite-enstatite field boundary and the coexisting vapor phase becomes richer in H_2O.

In the presence of mixed H_2O-CO_2 vapor all vapor-present reactions shown in Figure 4 become divariant rather than univariant. Thus the pair of reactions

Enstatite + H_2O → Forsterite + Liquid

and

Forsterite + Enstatite + CO_2 → Liquid

shown in Figure 4 simply represent the two extreme ends of one divariant surface in this system. In order to illustrate how quickly the vapor present along each divariant surface becomes water-rich, the contour for $X_{CO_2} = 0.2$ on three intersecting divariant surfaces has been plotted in Figure 4.

The transition with increasing pressure from vapor-present to vapor-absent melting in this system is illustrated by a series of isobaric sections through Figure 4. These are given in simplified form in Figure 5. The lines shown are the isobaric traces of the divariant

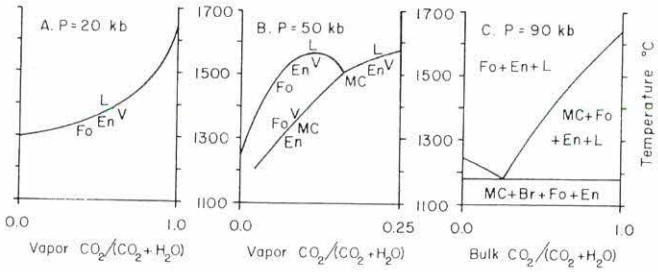

Figure 5. Isobaric sections through the system $MgO-SiO_2-H_2O-CO_2$ at 20, 50, and 90 kbar. The range of vapor compositions which may coexist with forsterite plus enstatite becomes smaller as pressure increases, until at 90 kbar forsterite plus enstatite can no longer coexist with vapor.

surfaces discussed above. Figure 5A shows that at 20 kbar forsterite plus enstatite may coexist with vapor of any X_{CO_2}. At 20 kbar CO_2 is relatively insoluble in the silicate liquid, and does not lower the melting point of the assemblage forsterite plus enstatite nearly as much as H_2O. Eggler (1975) concluded, in agreement with Mysen and Boettcher (1975a,b), that at 20 kbar the vapor-saturated liquid changes from quartz-normative to forsterite-normative as the X_{CO_2} of vapor becomes greater than 0.45.

The thermal maximum shown on reaction 6 at 50 kbar in Figure 5B is the same as that denoted by the heavy dashed line in Figure 4. The composition of the vapor at the thermal maximum changes rapidly from CO_2-rich at 40 kbar to H_2O-rich at 50 kbar. Figure 5B shows that forsterite plus enstatite cannot coexist with vapor richer in CO_2 than that at the isobaric invariant point schematically illustrated, where the subsolidus carbonation reaction intersects the solidus. At temperatures below the solidus the composition of the vapor coexisting with forsterite plus enstatite is buffered by the subsolidus reaction. At the solidus the compositions of both liquid and vapor are fixed. Above the solidus the composition of vapor coexisting with forsterite plus enstatite is buffered by reaction 6, until the temperature of the thermal maximum on that reaction is exceeded. At higher temperatures all vapor is dissolved in the liquid.

Figure 5C illustrates that at 90 kbar and temperatures below the solidus all volatiles are tied up in brucite and magnesite, in the presence of forsterite plus enstatite. A vapor phase is not stable in the presence of the assemblage forsterite plus enstatite. The first melting takes place at a quaternary eutectic involving forsterite, enstatite, brucite, and magnesite.

The P-T net constructed for the system $MgO-SiO_2-H_2O-CO_2$ provides the information necessary to construct isobaric liquidus diagrams, and from them to estimate geometrically the compositions of liquids formed at the solidus. The position of the surface of liquid compositions which coexist with forsterite and enstatite is shown at 20, 40, 70, and 90 kbar in Figure 6. The great change in the position of this surface is due to the increased solubility of CO_2 in the liquid associated with the intersection of reaction 5 with the solidus at about 42 kbar.

The estimated compositions of liquids formed at the solidus at pressures of 20, 50, and 90 kbar are listed in Table 1. These were estimated for a bulk composition consisting of forsterite plus enstatite plus a small amount of volatiles with a 3/1 H_2O/CO_2 ratio. At 20 kbar the first liquid is estimated to be quartz-normative, in agreement with the conclusions of Eggler (1975) and of Mysen and Boettcher (1975a, b). However, at a pressure of 50 kbar the fact that magnesite coexists with forsterite plus enstatite at the solidus causes the first liquid to be highly undersaturated with respect to silica, in fact periclase-forsterite normative. The involvement of magnesite in the melting reaction prevents the SiO_2-enrichment caused at low pressures by vapor with high H_2O/CO_2. At 90 kbar the first liquid coexisting with forsterite plus enstatite is estimated to be enstatite-forsterite normative. The existence of the quaternary eutectic relationship between forsterite, enstatite, brucite, and magnesite at pressures greater than 90 kbar requires that the compositions of the first liquids will be essentially constant at higher pressures, becoming slightly richer in MgO with increasing pressure.

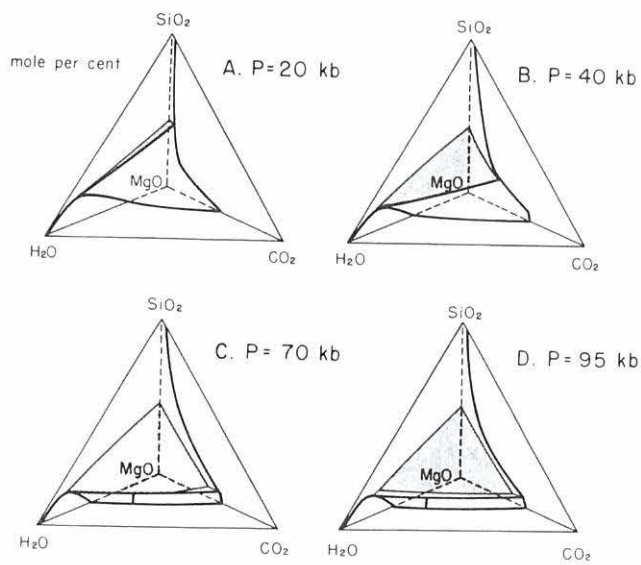

Figure 6. Partial isobaric liquidus diagrams for the system $MgO-SiO_2-H_2O-CO_2$. Heavy lines show liquidus field boundaries on the vapor-saturated liquidus surface. The surface of liquid compositions coexisting with forsterite plus enstatite is stippled. This is vapor absent, but reaches the vapor-saturated liquidus surface in Figures 6A, 6B, and 6C. As pressure increases the volatile-rich parts of the surface become increasingly silica-undersaturated.

TABLE 1. Geometrically estimated compositions of first liquids coexisting with forsterite plus enstatite in a bulk composition with an H_2O/CO_2 ratio of 3/1.

Pressure	Mole Percent				Weight Percent			
	MgO	SiO_2	H_2O	CO_2	MgO	SiO_2	H_2O	CO_2
20 kbar	12	17	70	1	18	37	45	0.x
50 kbar	34	10	31	25	38	17	15	30
90 kbar	32	18	39	11	36	31	19	14

Summary

The model developed for the system $MgO-SiO_2-H_2O-CO_2$ requires that in successively higher pressure ranges, three different types of melting processes characterize the melting of forsterite plus enstatite in the presence of H_2O-CO_2 vapor.

(1) At low pressures the melting reaction is either

Enstatite + Vapor → Forsterite + Liquid

at low X_{CO_2}, or

Forsterite + Enstatite + Vapor → Liquid

at high X_{CO_2}. The composition of the liquids produced varies from quartz-normative in the presence of H_2O to forsterite-normative in the presence of CO_2. This agrees with the conclusions of Eggler (1975) and Mysen and Boettcher (1975a,b). At 20 kbar H_2O is partitioned toward silicate liquids, and CO_2 is partitioned toward the coexisting vapor.

(2) At pressures between 42 and 80 kbar the important melting reaction is 4. The composition of the vapor phase taking part in this reaction is buffered by the subsolidus reaction 5. At temperatures above the solidus for the assemblage forsterite plus enstatite, a thermal maximum exists on the reaction

Forsterite + Enstatite + Vapor → Liquid.

The X_{CO_2} of the vapor at this thermal maximum becomes rapidly smaller as pressure increases.

(3) At pressures above 90 kilobars forsterite plus enstatite melt at a quaternary eutectic with brucite and magnesite, with no vapor present. H_2O/CO_2 of the liquid is fixed at about 3/1 by the eutectic between $Mg(OH)_2$ and $MgCO_3$.

The composition of the first liquid formed in bulk compositions of forsterite plus enstatite and a small amount of volatiles with a 3/1 H_2O/CO_2 ratio changes from quartz-normative to periclase-forsterite normative to enstatite-forsterite normative as pressure increases.

These three kinds of melting reaction must also occur in peridotite, where H_2O and CO_2 are present as vapor, or are stored in amphibole, phlogopite, and carbonate. The distribution of H_2O and CO_2 among liquid crystals and vapor in the simple system $MgO-SiO_2-H_2O-SiO_2$ provides a guide for interpretation of the phase relationships in the complex peridotite-H_2O-CO_2 system (Wyllie, this volume).

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